

## **Supporting Information for**

### **Occurrence and Sources of Radium in Groundwater Associated with Oil Fields in the Southern San Joaquin Valley, California**

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Table S4. Chemical and ancillary data for wells. (.xlsx)

## Section S1. Study Area Description

The study area is in Kern County, in the southern San Joaquin Valley (SJV) (Figure 1). The SJV is part of the Central Valley of California, a 700-km-long basin containing >7500 m of Mesozoic through Cenozoic-aged sediments.<sup>1</sup> From 2014 to 2017, water samples were collected from 40 water wells located in, or near (within 5 km), the Fruitvale (FV), Lost Hills (LH), and South Belridge (SB) oil fields (Figure 1, Table S1). The water-bearing units sampled on the east side of the SJV around the FV oilfield, and the water-bearing units sampled on the west side of the valley around the LH and SB oilfields, are part of the Central Valley regional aquifer system. Aquifer sediments on the east and west sides of the valley are derived from different sources, but they generally grade into each other along the axis of the valley.<sup>2</sup>

In the FV oil field, located on the east side of the SJV, the sampled wells are screened in semi-consolidated gravel, sand, silt, and clay in late Miocene to Pleistocene fluvial deposits in the Kern River Formation (Figure S1).<sup>3</sup> Those sediments were largely derived from granitic rocks in the Sierra Nevada to the east.<sup>4</sup> The aquifer sediments are semi-confined to confined.<sup>3</sup> The primary source of natural recharge to the aquifer is the Kern River, which flows across the southern part of the oil field (Figure 1). Depths to groundwater in the sampled water wells ranged from about 61 m to 79 m (median=71 m) (Table S1). Groundwater flow directions are generally to the west, southwest.<sup>3</sup> The median depth to the bottom of perforations in the sampled water wells is 209 m, whereas the median depth to the top of perforations in FV oil wells is 1088 m.<sup>5</sup> Sediments in the Kern River Formation and marine sediments in the underlying Etchegoin Formation are present between the deepest water wells and shallowest oil wells (completed in basal portions of the Etchegoin Formation) (Figure S1).<sup>6</sup> The Macoma Claystone, within the basal portion of the Etchegoin Formation, generally serves as a hydraulic barrier between the oil

and water-bearing zones.<sup>6</sup> Oil extraction in the FV oil field began in 1928.<sup>7</sup> The oil field contains about 320 oil-production and injection wells that are listed as active or newly drilled.<sup>8</sup> Oil production in the FV field is primarily from the Etchegoin, Chanac, and Santa Margarita Formations (Figure S1). From 1960 to 2017, about 87 million m<sup>3</sup> of oil-field water were injected into those formations,<sup>8</sup> primarily for water disposal.<sup>3</sup>

In the SB and LH oil fields, located on the west side of the SJV, the sampled wells are screened in sand, silt, and clay in Holocene/Pleistocene alluvium and fluvial, deltaic, to lacustrine deposits in the Tulare Formation (Pleistocene).<sup>9</sup> The sediments were largely derived from marine rocks in the Temblor Range to the west.<sup>9</sup> The aquifers are generally unconfined to semi-confined, except for water-bearing units in the Tulare Formation that are below the Corcoran Clay, which is an important confining layer on the west side of the SJV.<sup>2</sup> Natural sources of recharge are more limited on the west side of the SJV than on the eastside, but they include precipitation and stream flow in uplands to the west that infiltrates into the aquifers.<sup>2</sup> Depths to groundwater in the sampled water wells ranged from about 10 m to 121 m (median=69 m) (Table S1). Groundwater flow directions are generally to the northeast.<sup>2</sup> The median depths to the bottom of perforations in the sampled water wells are 199 m (LH) and 153 m (SB), whereas the median depths to the top of perforations in oil wells are 414 m (LH) and 326 m (SB).<sup>5</sup> Within the LH and SB oil fields, the deepest water wells and shallowest oil wells are both completed in the Tulare Formation (Figure S1), although the Tulare oil wells in the vicinity of the sampled Tulare water wells are deeper than the water wells. In parts of LH and SB, the Amnicola, Tulare, and Corcoran Clays (deepest to shallowest) in the Tulare Formation could serve as confining layers between the oil wells and water wells.<sup>2,9</sup> Nevertheless, the close vertical proximity of the wells indicates natural mixing between oil-field formation water and fresher groundwater could

occur. Oil extraction in the LH and SB oil fields began in the early 1910s.<sup>10,11</sup> The number oil-production and injection wells that are listed as active or newly drilled range from about 5,500 in LH to 11,700 in SB.<sup>8</sup> Oil production is primarily from the Temblor, Monterey, Etchegoin, and Tulare Formations (Figure S1). From 1960 to 2017, about 435 million m<sup>3</sup> (LH) and 1400 million m<sup>3</sup> (SB) of oil-field water were injected into these formations.<sup>8</sup> From 2014 to 2017 in LH, ~87% and ~13% of the injected water was for enhanced oil recover (EOR) and water disposal, respectively. From 2014 to 2017 in SB, ~56% and ~44% of the injected water was for EOR and water disposal, respectively.<sup>8</sup>

## **Section S2. Analysis of Radium in Sediment**

Activities of <sup>228</sup>Ra and <sup>226</sup>Ra in aquifer sediment collected from the LH and SB boreholes (Figure 1) were measured using the method of Lauer et al. (ref 12). Briefly, the sediment was washed with deionized water to remove drilling mud and the >63-μm fraction was retained for analysis. The retained fraction was dried (110°C) for 24 hours and ground to a diameter <5 mm. Dried and crushed sediment samples were packed in plastic Petri style dishes (6.5 cm diameter and 2 cm height) that were then sealed with electrical tape and coated in wax to prevent escape of <sup>220</sup>Rn and <sup>222</sup>Rn. Sealed samples were incubated for at least 21 days to allow <sup>226</sup>Ra to reach secular equilibrium with <sup>222</sup>Rn, <sup>214</sup>Bi, and <sup>214</sup>Pb; and for <sup>228</sup>Ra to reach secular equilibrium with <sup>228</sup>Ac. After incubation, samples were counted on a Canberra Broad Energy 5030 Germanium Gamma detector at Duke University. Samples were typically counted for 6 to 48 hours so counting errors (2σ) were <10%. <sup>226</sup>Ra activities were measured through the 351 keV energy peak of <sup>214</sup>Pb. <sup>228</sup>Ra activities were measured through the 911 keV energy peak of <sup>228</sup>Ac. Detector efficiencies were determined using a U-Th reference ore material (DL-1a) prepared by

the Canadian Certified Reference Materials Project that was packaged and incubated in a container identical to the samples. Background and efficiency checks were performed prior to and during the period of sample analysis. The data are listed in Table S5 and ref 13.

$^{228}\text{Ra}$  and  $^{226}\text{Ra}$  activities in the sediment range from 8.3 to 32.5 Bq/kg and 7.5 to 52.6 Bq/kg, respectively (Table S5). The Th and U contents of the sediments can be back calculated assuming secular equilibrium between  $^{228}\text{Ra}$ - $^{232}\text{Th}$  and  $^{226}\text{Ra}$ - $^{238}\text{U}$ , respectively, and applying these conversion factors: 1 Bq  $^{232}\text{Th}$ /kg = 245  $\mu\text{g/kg}$  Th; 1 Bq  $^{238}\text{U}$ /kg = 81  $\mu\text{g/kg}$  U. Based on those calculations, the Th and U contents of the sediments range from 2030 to 7960  $\mu\text{g/kg}$  and 608 to 4260  $\mu\text{g/kg}$ , respectively.

### **Section S3. Additional Analysis of Groundwater Mixing with Oil-Field Water**

Based on the mixing analysis presented in the article, the high-Ra samples are grouped into 4 categories; (1) highly mixed, surface source of oil-field water (BG4a, BG7), (2) slightly mixed, subsurface source of oil-field water (LG3, LG9), (3) highly mixed, surface and subsurface sources of oil-field water (BG5), and (4) little or no mixing with oil-field water (LG2, LG6). Data for  $\text{NH}_4$ , DOC, VOCs,  $\delta^2\text{H-CH}_4$ ,  $\delta^{13}\text{C-CH}_4$ , and  $\delta^{13}\text{C-DIC}$  provide additional understanding of mixing between groundwater and oil-field water in the seven Lost Hills and South Belridge samples with elevated  $^{226}\text{Ra}+^{228}\text{Ra}$  activities.

Group 1 contains the two samples with the highest Ra activities in the South Belridge oil field, BG4a and BG7. Oil-field water in these samples is from unlined oil-field water disposal ponds upgradient from the wells. BG4a and BG7 contain substantially more DOC (39 and 29 mg/L, respectively) than other South Belridge groundwater that is unaffected by mixing with oil-field water (median=0.7 mg/L) (Figure S4), and both samples contain benzene (BG7 also

contains toluene), consistent with oil-field water. BG4a and BG7 both contain low concentrations of CH<sub>4</sub> and NH<sub>4</sub>. Concentrations of CH<sub>4</sub> (0.16 to 1.25 mole %) and NH<sub>4</sub> (<0.01 to 0.24 mg N/L) in BG4a and BG7 are minor compared to the amounts in Belridge oil-field water (CH<sub>4</sub>, 85 to 87 mole %) (NH<sub>4</sub>, 118 to 460 mg N/L) (Figure S6B), even though the groundwater samples contain ~40 to 45% oil-field water. The discrepancy could be explained by CH<sub>4</sub> degassing and NH<sub>4</sub> oxidation in the open-air pond environment. NH<sub>4</sub> oxidation would produce NO<sub>3</sub>. Both samples contain NO<sub>3</sub> (6.1 to 6.9 mg N/L), although some NO<sub>3</sub> produced by NH<sub>4</sub> oxidation could have been removed by denitrification in the anoxic groundwater (O<sub>2</sub> ≤0.2 mg/L).

Group 2 contains the two samples with the highest Ra activities in the LH oil field, LG3 and LG9. Oil-field water in these samples appears to be from subsurface sources rather than pond leakage. Unlike the samples affected by pond leakage, LG3 and LG9 contain high concentrations of CH<sub>4</sub> (33 to 79 mole %) and NH<sub>4</sub> (19.7 to 21.5 mg N/L) and no nitrate.  $\delta^2\text{H}$ -CH<sub>4</sub> and  $\delta^{13}\text{C}$ -CH<sub>4</sub> values in both samples are essentially identical to thermogenic gas in Lost Hills oil-field water, whereas the isotopic composition of the small amount of CH<sub>4</sub> in BG7, which was affected by pond leakage, is more diagnostic of biogenic CH<sub>4</sub> from fermentation processes commonly associated with near-surface environments that has been affected by oxidation (Figure S6A). The presence of benzene and toluene in both samples also suggests mixing with oil-field water. LG3 and LG9 also have highly enriched  $\delta^{13}\text{C}$ -DIC values like LH oil-field water (Figure S6B).

Group 3 consists of one sample from SB, BG5, that is ~0.5 km downgradient from an unlined disposal pond that operated from the 1950s until 2006. BG5 contains benzene.  $^3\text{H}$  and VOC data indicate some water in BG5 was in relatively recent contact with the land surface. BG5 contains the highest  $^3\text{H}$  concentration (0.6 TU) among the LH and SB groundwater

samples, and it also contains methyl tertiary-butyl ether (MTBE) (0.27 µg/L), a manufactured compound banned in California beginning in 2004.<sup>14</sup> Like BG4a and BG7, BG5 contains elevated DOC (37 mg/L). Unlike BG4a and BG7, BG5 contains elevated CH<sub>4</sub> (24 mole %; isotopically like Belridge oil-field gas, Figure S6A) and NH<sub>4</sub> (18.4 mg N/L) concentrations, no nitrate, enriched δ<sup>13</sup>C-DIC (Figure S6B), and large numbers of oil-production and injection wells and injection volumes within 500 m, like the Lost Hills samples affected by subsurface sources of oil-field water (Table S1). The data indicate BG5 could contain oil-field water from surface and subsurface sources.

Group 4 consists of two samples from LH, LG2 and LG6. Water-isotope, Cl, Br, and Li data indicate those samples contain little or no oil-field water, consistent with the low CH<sub>4</sub>, NH<sub>4</sub>, and DOC concentrations and absence of benzene and toluene in the samples. LG2 and LG6 also have depleted δ<sup>13</sup>C-DIC values, like other regional groundwater unaffected by mixing with oil-field water (Figure S6B).

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## Figures

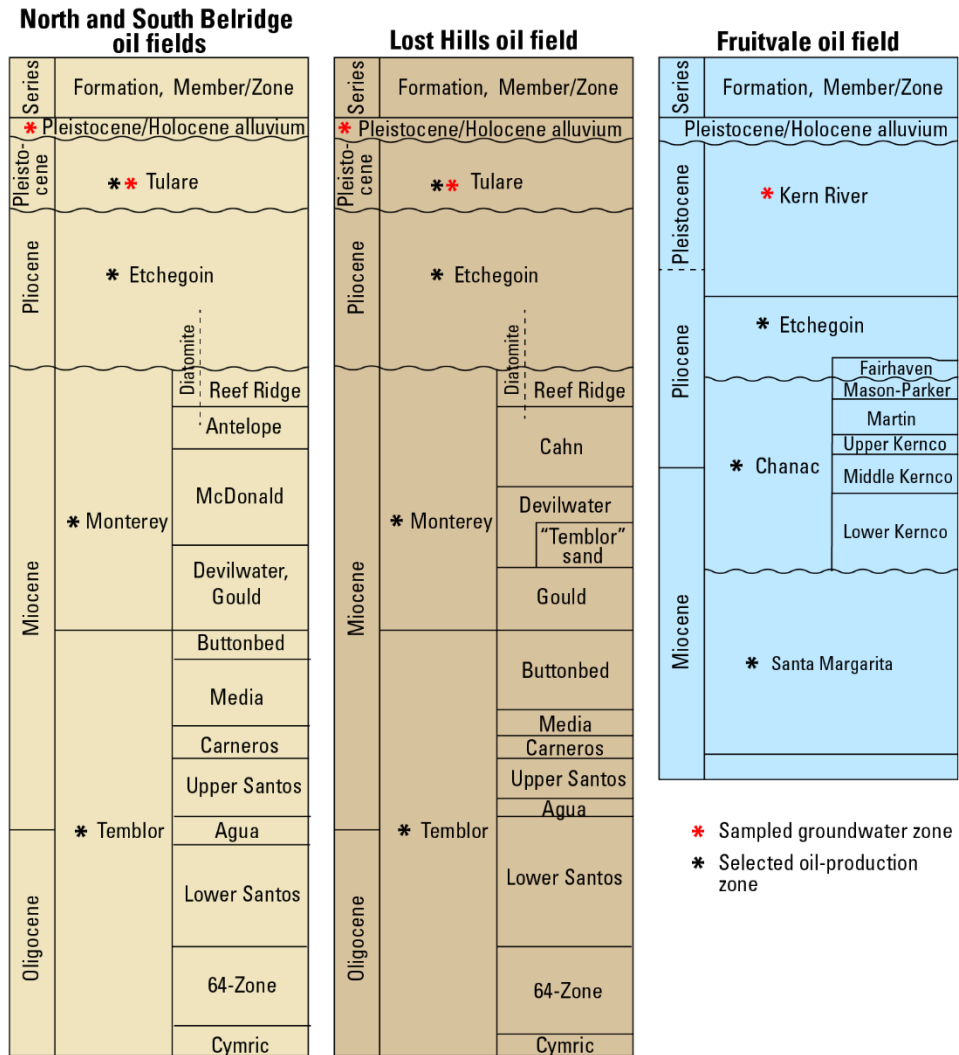


Figure S1. Generalized stratigraphic relations in the studied oil fields, modified from refs 1, 10–11, 15–17.

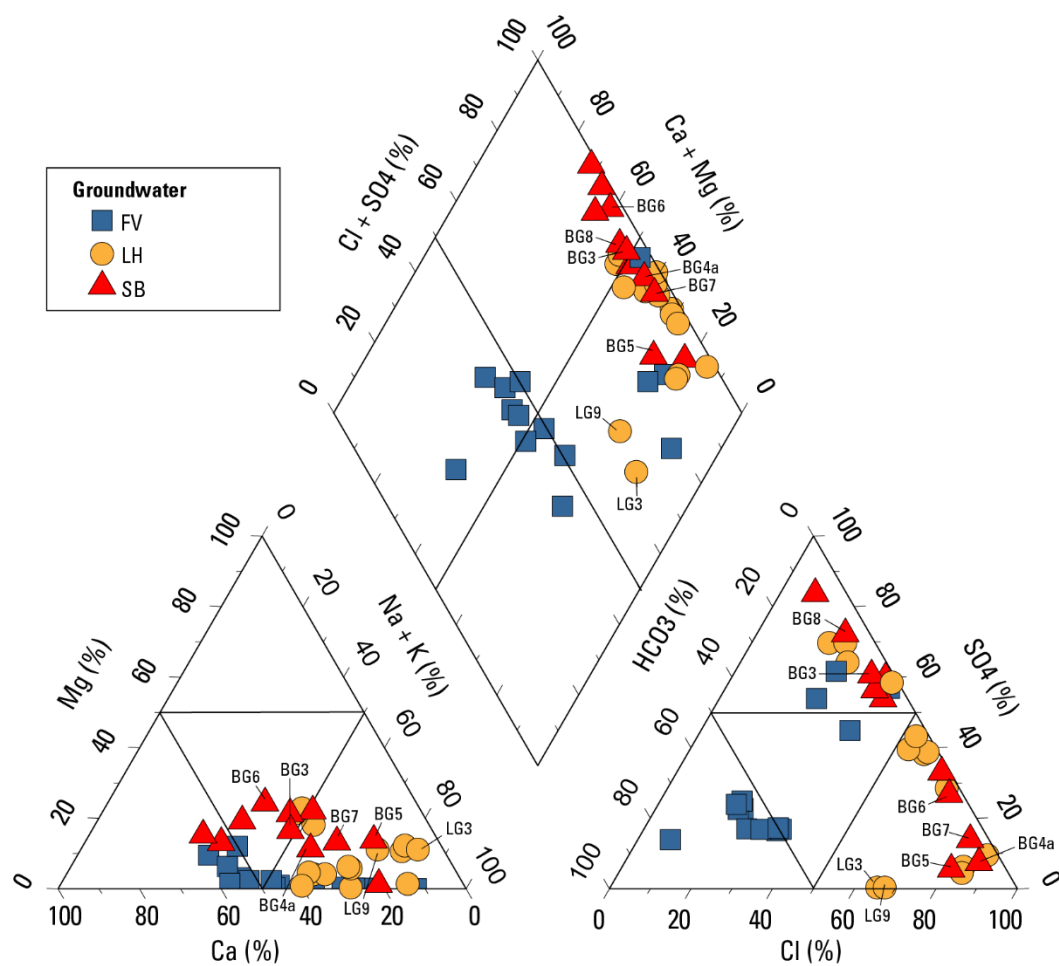


Figure S2. Major-ion composition of groundwater.

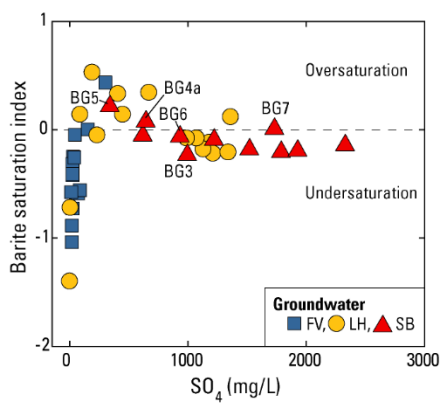


Figure S3. Barite saturation index in relation to sulfate concentration in groundwater. The higher  $\text{SO}_4$  concentrations in LH and SB, compared to FV, are accompanied by greater barite saturation

indexes. Despite the high potential for secondary barite co-precipitation and associated removal of Ra, groundwater in the LH and SB oil fields has high Ra, indicating the geochemical conditions that enhance Ra mobilization are more effective than Ra retention by secondary processes.

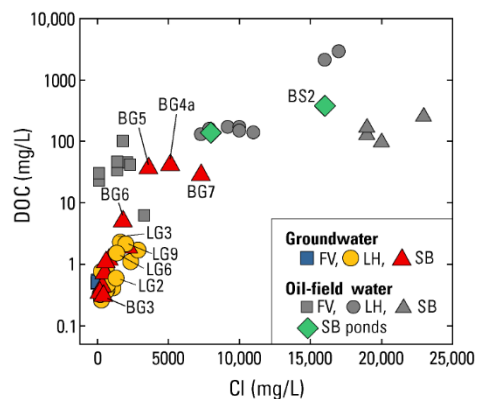


Figure S4. Concentrations of dissolved organic carbon in relation to chloride concentrations in groundwater and oil-field water. Data for oil-field water from refs 18, 19.

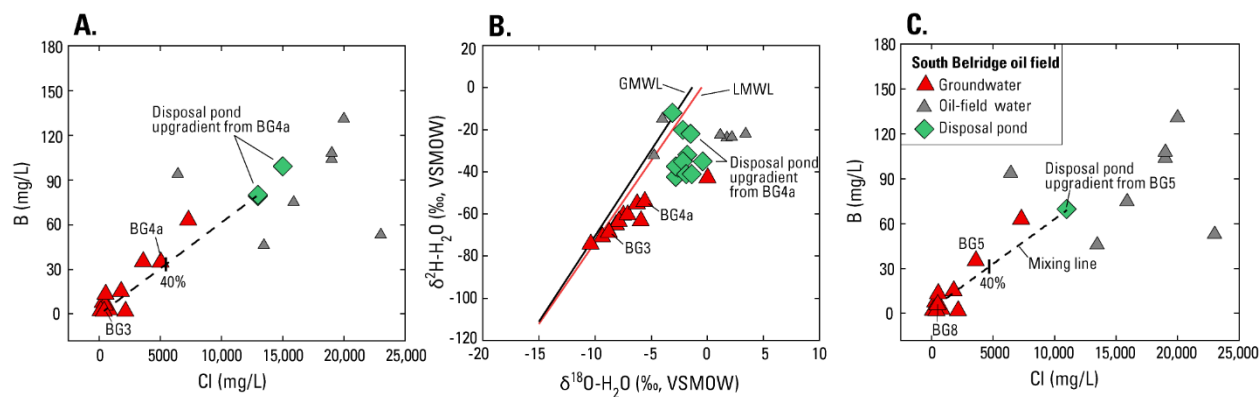


Figure S5. (A) and (C) concentrations of boron in relation to chloride concentrations in selected samples, (B)  $\delta^2\text{H-H}_2\text{O}$  in relation to  $\delta^{18}\text{O-H}_2\text{O}$ . Data for oil-field water from refs 18, 19. In (A) and (B), data for disposal pond from ref 20, data for Global Meteoric Water Line and Local Meteoric Water Line from refs 21 and 22, respectively. In C, data for disposal pond from ref 23.

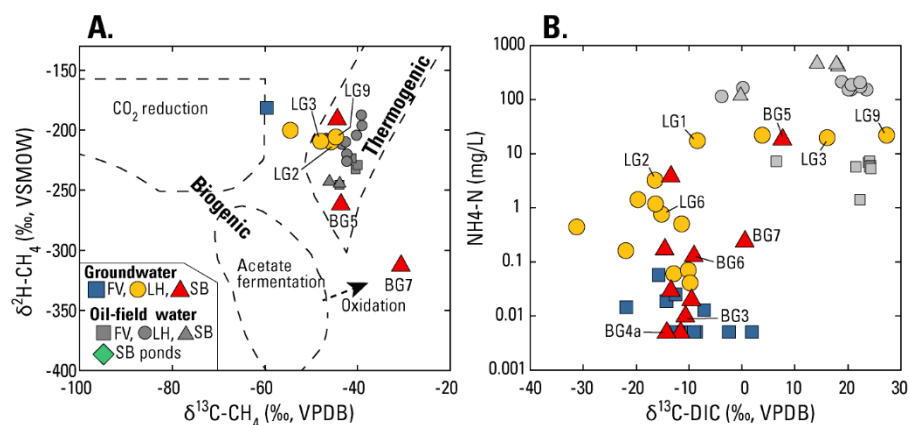


Figure S6. (A)  $\delta^2\text{H-CH}_4$  in relation to  $\delta^{13}\text{C-CH}_4$  and (B) concentrations of ammonium in relation to  $\delta^{13}\text{C-DIC}$ . Data for oil-field water from refs 18, 19. In (A), methane source boundaries from refs 24, 25.

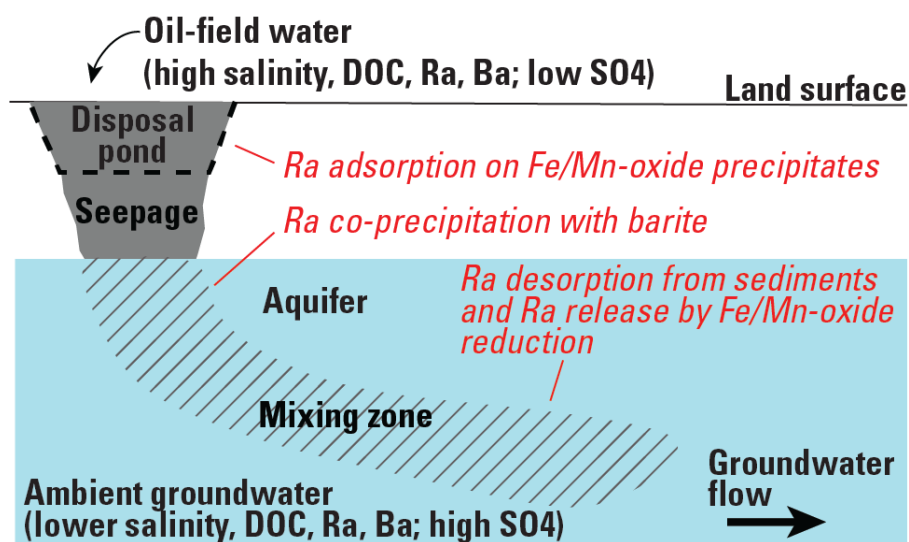


Figure S7. Conceptual model of radium demobilization in near-pond environment and radium mobilization in downgradient zone of mixing between pond seepage and ambient groundwater. Not to scale.



Table S1. Construction and ancillary data for sampled water wells. Data on water wells from refs 26-28. Data on oil-field infrastructure from ref 8.  
[na, not applicable; nd, no data]

Well name	Project ID	Well type	Depth to top of perforations (m)	Depth to bottom of perforations (m)	Well depth (m)	Depth to water (m)	Aquifer or other sample type	Number of Plugged and Buried oil and gas wells within 500 m	Number of oil and gas production wells within 500 m	Number of injection wells within 500 m	Cumulative injection volume within 500 m (m3), (injection period)	Median depth to top of perforations in oil and gas wells within 500 m (m)
FG1	4_FRUT_ZR_01	Public supply well	128.0	213.4	219.5	79.2	Alluvium	0	0	0	0 (na)	na
FG2	4_FRUT_ZR_02	Public supply well	137.2	213.4	219.5	nd	Alluvium	38	39	3	1,134,432 (1978-1994)	1263
FG3	4_FRUT_ZR_03	Public supply well	118.3	219.8	219.8	nd	Alluvium	9	9	1	303,030 (1982-1998)	1283
FG4	4_FRUT_ZR_04	Public supply well	118.9	210.3	216.4	nd	Alluvium	15	22	0	0 (na)	1054
FG5	4_FRUT_ZR_05	Public supply well	140.2	213.4	219.5	72.5	Alluvium	2	2	0	0 (na)	1615
FG6	4_FRUT_ZR_06	Public supply well	79.2	207.3	213.4	65.2	Alluvium	2	2	0	0 (na)	1423
FG7	4_FRUT_ZR_07	Public supply well	125.0	204.2	210.3	74.4	Alluvium	5	4	1	189,205 (1977-1983)	1315
FG8	4_FRUT_ZR_08	Public supply well	74.4	243.8	243.8	71.6	Alluvium	5	5	0	0 (na)	1316
FG9	4_FRUT_ZR_09	Public supply well	82.3	182.9	182.9	61.3	Alluvium	10	10	1	0 (1985-1986)	1141
FG10	4_FRUT_ZR_10	Public supply well	115.8	213.4	219.5	70.4	Alluvium	0	0	0	0 (na)	na
FG11	4_FRUT_ZR_11	Public supply well	106.7	182.9	206.7	72.8	Alluvium	2	2	0	0 (na)	1329
FG12	4_FRUT_ZR_12	Public supply well	77.1	172.5	253.9	nd	Alluvium	1	1	0	0 (na)	2509
FG13	4_FRUT_ZR_13	Industrial supply well	155.1	198.1	198.1	66.4	Alluvium	10	25	10	15,882,280 (1979-2017)	1329
FG14	4_FRUT_ZR_14	Domestic well	128.0	146.3	152.4	61.5	Alluvium	40	43	1	736,880 (1978-1984)	1267
BG1	BELS-01	Monitoring well	79.7	94.5	96.0	54.6	Alluvium	138	137	86	17,434,688 (1977-2017)	344
BG2	BELS-02	Public supply well	112.8	182.9	185.9	nd	Tulare	0	0	0	0 (na)	na
BG3	BELS-03	Irrigation well	nd	nd	nd	nd	nd	0	0	0	0 (na)	na
BG4a	4_BELS_EXP-01	Monitoring well	85.3	91.4	93.0	nd	Alluvium	0	0	0	0 (na)	na
BG4b	BELS-04	Monitoring well	103.6	120.4	121.9	61.6	Tulare	0	0	0	0 (na)	na
BG5	BELS-05	Monitoring well	155.4	167.6	167.6	69.4	Tulare	166	519	381	38,066,876 (1977-2017)	351
BG6	BELS-06	Irrigation well	76.2	153.0	153.0	nd	Tulare	0	0	0	0 (na)	na
BG7	BELS-07	Irrigation well	74.7	165.2	176.8	83.1	Tulare	2	12	0	0 (na)	1,570
BG8	BELS-08	Monitoring well	161.5	192.0	195.1	74.7	Tulare	428	517	246	18,336,993 (1977-2018)	342
BG9	BELS-09	Monitoring well	99.4	102.4	103.6	69.2	Alluvium	235	354	182	8,974,959 (1978-2018)	331
BG10	BELS-10	Monitoring well	77.7	86.9	86.9	58.6	Alluvium	390	553	197	27,574,071 (1977-2018)	430
BS2	4_BELS_PW02	Oil-field water disposal pond	na	na	na	na	Oil-field water disposal pond	1	3	0	na	nd
BS3	4_BELS_PW03	Oil-field water disposal pond	na	na	na	na	Oil-field water disposal pond	0	0	1	na	nd
LG1	LOST-01	Monitoring well	194.2	233.2	302.7	114.9	Tulare	99	180	81	19,171,918 (1977-2017)	571
LG2	LOST-02	Oil field water supply	143.3	320.0	356.6	nd	Tulare	2	0	0	0 (na)	nd
LG3	LOST-03	Monitoring well	225.9	231.6	233.2	120.9	Tulare	93	211	106	19,065,515 (1989-2017)	nd
LG4	LOST-04	Oil field water supply	128.0	257.6	317.0	nd	Tulare	1	0	0	0 (na)	nd
LG5	LOST-05	Monitoring well	137.2	149.4	185.3	88.2	Tulare	1	12	1	91,789 (1990-2017)	nd
LG6	LOST-06	Irrigation well	nd	nd	nd	nd	nd	0	0	0	0 (na)	na
LG7	LOST-07	Irrigation well	61.0	176.8	178.3	nd	Tulare	0	0	0	0 (na)	na
LG8	LOST-08	Irrigation well	97.5	207.3	207.3	nd	Tulare	0	0	0	0 (na)	na
LG9	LOST-09	Monitoring well	191.2	196.9	198.4	nd	Tulare	62	113	52	9,785,578 (1999-2017)	nd
LG10	LOST-10	Monitoring well	85.3	91.4	91.4	10.5	Alluvium	0	0	0	0 (na)	na
LG11	LOST-11	Monitoring well	61.0	67.1	67.1	12.0	Alluvium	1	1	0	0 (na)	nd
LG12	LOST-12	Irrigation well	103.6	201.2	201.2	nd	Tulare	0	0	0	0 (na)	na
LG13	LOST-13	Test well	167.6	176.8	176.8	nd	Tulare	0	0	0	0 (na)	na
LG14	LOST-14	Test well	125.0	134.1	134.1	nd	Alluvium	0	0	0	0 (na)	na
LG15	LOST-15	Oil field water supply	133.8	255.1	280.4	nd	Tulare	247	424	191	na	nd
LP6	4_LOST_PW06	Oil-field injectate	na	na	na	na	Oil-field injectate	128	233	106	na	571

Table S2. Sample collection methods.

Analyte group	Sampling method	Bottles	Rinse	Filter	Preservative	Storage	Reference
Field parameters: temperature, dissolved oxygen, specific conductance, pH, turbidity, sulfide	Monitor until stability criteria reached during well purging	none	3 casing volumes	none	none	none	29
Volatile organic compounds (VOCs)	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	3 40-mL amber glass, no headspace	3 volumes, bottom fill	none	Acidify to pH<2 with 1:1 HCl	chill	30, 31
Dissolved organic carbon (DOC)	Collected from short non- methanol rinsed teflon tubing in a chamber bag at the wellhead	250-mL baked amber glass	1 volume, bottom fill	0.45 micron	Acidify to pH<2 with 4.5N H <sub>2</sub> SO <sub>4</sub>	chill	30, 32
Major and minor ions, trace elements, alkalinity	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	250 ml clear HDPE	yes	none	none	chill	30
		250 ml clear HDPE	yes	0.45 micron	Acidify to pH<2 with 7.5 N HNO <sub>3</sub>	chill	
		250 ml clear HDPE	yes	0.45 micron	none	chill	
Nutrients	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	125 ml brown HDPE	yes	0.45 micron	none	chill	30
Stable isotopes of hydrogen ( $\delta^2\text{H}$ ) and oxygen ( $\delta^{18}\text{O}$ ) in water	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	60-mL glass with polyseal cap	none	none	none	ambient	33, 34
$\delta^{13}\text{C}$ of inorganic carbon dissolved in water and carbon-14 abundance	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	1-L coated clear glass with polyseal cap, no headspace	3 volumes, bottom fill	0.45 micron	none	chill	30
Tritium	Collected from short non- methanol rinsed teflon tubing in a chamber bag at the wellhead	1-L HDPE with polyseal cap, no headspace	Bottom fill	none	none	ambient	30
Radium-224 and radium- 226	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	1-L HDPE	3 volumes	0.45 micron	Acidify to pH<2 with 7.5 N HNO <sub>3</sub>	ambient	30
Radium-228	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	2 1-L HDPE	3 volumes	0.45 micron	Acidify to pH<2 with 7.5 N HNO <sub>3</sub>	ambient	30
Dissolved noble gases	Collected at the wellhead	2 copper tubes, no bubbles, crimped	minimum 10 tube volumes	none	none	ambient	35, 36
Dissolved hydrocarbon gases, $\delta^{13}\text{C}$ & $\delta^2\text{H}$ of methane	Collected from short non-methanol rinsed teflon tubing in a chamber bag at the wellhead	Isoflask	none	none	biocide	ambient	37, 38

Table S3. Laboratory analytical methods. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Analyte group	Analytical method	Laboratory	Reference
Field parameters: temperature, dissolved oxygen, specific conductance, pH, turbidity, sulfide	Calibrated field meters and test kits	USGS field measurement	29
Volatile organic compounds (VOCs)	Purge and trap capillary gas chromatography/mass spectrometry (EPA Method 524.2)	USGS National Water-Quality Laboratory, Lakewood, Colorado	31
Dissolved organic carbon (DOC)	High-temperature combustion catalytic oxidation (EPA 415.3 rev 1.2)	USGS Organic Matter Research Laboratory, Sacramento, California	32, 39, 40
Major and minor ions, trace elements, alkalinity	Atomic absorption spectrometry, colorimetry, ion-exchange chromatography, inductively-coupled plasma atomic-emission spectrometry and mass spectrometry	USGS National Water-Quality Laboratory, Lakewood, Colorado	41-47
Nutrients	Kjedahl digestion, colorimetry by enzymatic reduction	USGS National Water-Quality Laboratory, Lakewood, Colorado	42, 48
Stable isotopes of hydrogen ( $\delta^2\text{H}$ ) and oxygen ( $\delta^{18}\text{O}$ ) in water	Gaseous hydrogen and carbon dioxide--water equilibration and stable-isotope mass spectrometry	USGS Stable Isotope Laboratory, Reston, Virginia	33, 34, 49-51
$\delta^{13}\text{C}$ of inorganic carbon dissolved in water and carbon-14 abundance	Stable isotope ratio mass spectrometry and accelerator mass spectrometry	Woods Hole Oceanographic Institution, National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS), Woods Hole, Massachusetts	52-57
Tritium	Electrolytic enrichment and gas counting	USGS Stable Isotope and Tritium Laboratory, Menlo Park, California	58
Radium-224 and radium- 226	Alpha spectroscopy (EPA method 903.1)	ALS Laboratories, Fort Collins, Colorado	59
Radium-228	Gas proportional counting (EPA method 904.0)	ALS Laboratories, Fort Collins, Colorado	59
Dissolved noble gases	Mass spectrometry	USGS Noble Gas Laboratory, Denver, CO	60
Dissolved noble gases	Mass spectrometry	Noble Gas Laboratory, Univ. of Oxford, Oxford, U.K.	61-64
Dissolved hydrocarbon gases, $\delta^{13}\text{C}$ & $\delta^2\text{H}$ of methane	Gas chromatography, Stable isotope ratio mass spectrometry	Weatherford (formerly Isotech) Laboratories	37, 38

Table S5. 226Ra and 228Ra activities in sediment samples collected from the LH and SB boreholes. Data can be downloaded from ref 13 using the site numbers, sample dates, and sample times listed in the table.

Sample name	Site number	Sample date	Sample time	Aquifer/Formation	Depth (m)	Ra-226 (Bq/kg)	Ra-228 (Bq/kg)	228Ra/226Ra Activity Ratio
BR-110	353049119434101	7/7/2018	1100	Alluvium	33.5	11.4	8.3	0.73
BR-160	353049119434101	7/7/2018	1700	Alluvium	48.8	10.8	10.0	0.92
BR-260	353049119434101	7/8/2018	1400	Alluvium	79.2	16.0	13.7	0.86
BR-310	353049119434101	7/8/2018	1500	Tulare	94.5	52.6	32.5	0.62
BR-340	353049119434101	7/8/2018	1700	Tulare	103.6	7.5	10.2	1.36
BR-410	353049119434101	7/9/2018	1000	Tulare	134.5	40.0	10.2	0.26
LH-40-50	354048119445001	3/8/2018	1300	Alluvium	12.2 - 15.2	19.8	17.6	0.89
LH-220	354048119445001	3/9/2019	1100	Alluvium	67.1	11.2	14.1	1.26
LH-380	354048119445001	3/9/2018	1600	Tulare	115.8	8.3	11.5	1.39
LH-480	354048119445001	3/10/2018	1100	Tulare	146.3	20.0	10.2	0.51